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April 5, 1957

Subject: Requirement for Additional Funds and
Extension of Period of Work)

Reference:

Task No. 1
Task No. 2

25X1

Dear Sir:

As was discussed with the cognizant Contract Administrator for your office on March 27, 1957 and in accordance with Article 4 of the contract, this is to advise you that by June 1, 1957 we will require additional funds beyond those presently provided for Item a, above. This requirement is estimated at

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In addition, we require immediate extension for the work required under Item b, above, to June 30, 1957, in order to continue the work on this program.

In view of the short time remaining on each of these programs, we would appreciate expeditious handling of these requests.

Very truly yours,

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Contract Administration

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January 8, 1959

EP up 25X1
CWS us

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T.O. 8 25X1

Subject: Quarterly Report No. 2

Reference: Contract [redacted]
Task Order No. 2

Power Sources Study No. 1

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Dear Sir:

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Enclosed herewith are three (3) copies of the UNCLASSIFIED Quarterly Report No. 2 of Task Order No. 2, covering the period of 1 September through 30 November 1956, that you requested yesterday from [redacted]

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Will keep you posted on progress of fabrication of the item called for by this Task Order so that you may plan your next visit.

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If additional information is required, please contact the undersigned.

Very truly yours,

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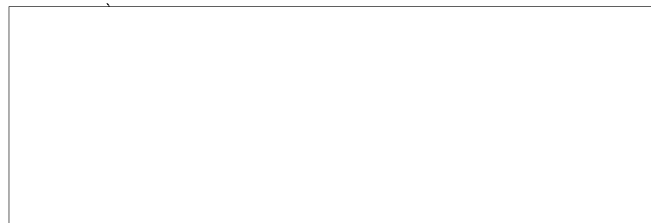
cc: Contracting Officer

Encs. - 3 UNCLASSIFIED Reports

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QUARTERLY REPORT NO. 2

on the

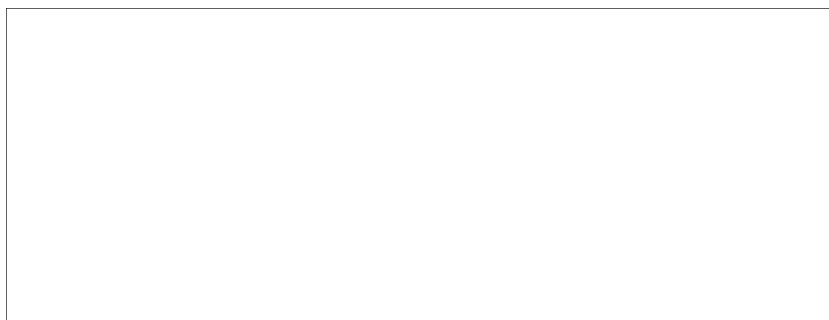
POWER SOURCES STUDY

Period: September 1, 1956 to November 30, 1956

Reference:



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I. PURPOSE OF THE STUDY

The purpose of this study is to increase the body of knowledge of potential portable electrical energy sources, as well as to develop two specific new devices. To achieve these ends, there are three portions to the program.

A. The first is a study of the literature, of progress made in the field at other installations and throughout the entire electrical energy-source industry, and of the applicability of known systems to the special requirements of portable, lightweight electrical energy sources.

B. The second portion of the program consists of the development of a thermoelectric generator, capable of wide utility in the field with a minimum of auxiliary equipment.

C. The third portion of the program consists of the development of a gas-activated battery system with the inherent advantages of extremely long shelf-life and great portability. X

II. ABSTRACT

Results of the first portion of an intensive study of a foreign kerosene-powered thermoelectric generator are reported. The efficiency of the device for converting thermal energy into electrical energy was found to be about 0.9 per cent.

Information gleaned from the current Russian periodical literature concerning criteria for the best thermoelements is discussed. Russian workers appear to have developed thermocouples for thermoelectric power generation with an effectiveness twice that of those available in the United States. The best Russian thermocouples for Peltier cooling applications are also about twice as effective as are those known to be available in this country.

Studies of heat transferred to a thermoelectric generator from sources of heat available in the field have shown the original figure of 1000 watts of thermal flux to be unattainable. Choosing the more-realistic value of 600 watts, a complete design for a thermoelectric generator, utilizing zinc antimonide and Advance as its elements, has been completed. Producing a maximum of 20.4 watts, the generator would be capable of yielding a current of 3.00 amperes with an electromotive force of 6.80 volts. The open-circuit voltage would be 13.60 volts.

Impurities in raw materials for production of zinc antimonide have made additional laboratory purification by means of zone melting essential. The process removes large amounts of sulfur from the antimony, but has an effect little better than re-casting on the zinc.

A description of an equipment for measurement of resistivity, built during the quarter, is presented. Equipment being designed for measurement of other thermal and electrical properties of thermocouples and materials used therein is enumerated.

Preliminary experiments, aimed toward the development of a gas-activated, solid-electrolyte battery, are described and results discussed. X

III. REPORTS AND CONFERENCES

A. Reports

With the exception of two monthly reports (numbers 3 and 4), no memoranda or reports were sent to the Customer during the quarter. The reason lies in the concentration upon laboratory work and study of documents, none of which has as yet reached a stage at which a separate report can be prepared.

B. Conferences

1. On October 1 - 3, 1956, attended the meeting of the Electrochemical Society in Cleveland, Ohio. In addition to hearing papers dealing with conventional battery systems, they heard some concerning semiconductors, which were of interest. While on a guided tour of the Research Laboratories of the National Carbon Company, the staff was able to observe the laboratories devoted to study of the silver/silver iodide/iodine solid-electrolyte battery, to development of fuel cells, and to investigation of batteries containing polymeric electrolytes. Although interesting in a general way, little specific information could be gained on the tour.

While at the Electrochemical Society meeting, an extended discussion of the general subject of thermoelectric generators took place with Dr. E. Mooser, of the Physical Institute ETH, Zurich, Switzerland, and Dr. T. C. Harman, of Battelle Memorial Institute, Columbus, Ohio. Dr. Mooser recounted his impressions of a paper presented in Ottawa, Ontario, by the Russian Academician A.F. Ioffe concerning the status of Russian work on thermoelectric generators and Peltier coolers. Dr. Mooser recalled that Ioffe had stated that the Russians are able to convert solar energy to electrical energy with an efficiency of ten per cent. (The Ottawa Citizen for September 15, 1956, quotes the same figure from Ioffe's remarks.) Mooser pointed out that Ioffe had never revealed

the composition of the efficient thermocouple. When pressed on this point, Mooser said, Ioffe became quite evasive. He did reveal, however, that an approach to improving the efficiency of thermoelements might be to prepare mixtures of compound semiconductors--he cited mercury selenide and mercury telluride as examples--and to investigate their properties. Neither the Swiss group nor that at Battelle had any information concerning mixtures of that type, but it was agreed that the suggestion might prove to be a fruitful one. X

2. On October 11 and on October 25, 1956, representatives of the Customer visited the Laboratory. On the basis of information reported in the section on "Factual Data", below, it was decided to reduce the proposed power input to the thermoelectric generator from 1000 watts to 600 watts. Several reports of European progress in the fields of fuel cells and thermoelectric generators were given to the staff of the Study at these meetings.

IV. FACTUAL DATA

A. Introduction

During the quarter, work in the laboratory was devoted to all three portions of the program. Major emphasis was placed on investigation of the properties of a foreign thermoelectric generator received by us for study on November 1, 1956. Preparation of materials for our own generator was begun, and design and construction of equipment for studying the properties of these materials was continued. Finally, some initial experiments on the gas-activated solid-electrolyte battery were performed.

B. Study Program

Most of the effort on this portion of the program was devoted to investigation of the foreign thermoelectric generator. However, a portion of the time was spent in study of translations of the current Russian periodical literature concerning thermoelectricity and Peltier cooling. Some of the information gleaned from this reading is reported at the end of this section.

1. Foreign Thermoelectric Generator

The plan for investigation of the foreign thermoelectric generator has been designed to provide the maximum amount of information without destroying the device. However, after as much information as is possible has been garnered from study of the complete assembly, it is planned to disassemble it, and to perform chemical and spectroscopic analyses upon its several parts.

The complete plan follows:

Step 1: Putting the generator and the radio for which it is designed into operation according to the directions of the manufacturer, observing performance of the complete assembly under these conditions.

Step 2: Measurement of the voltage and power output and the efficiency of conversion of thermal energy to electrical energy by the generator itself.

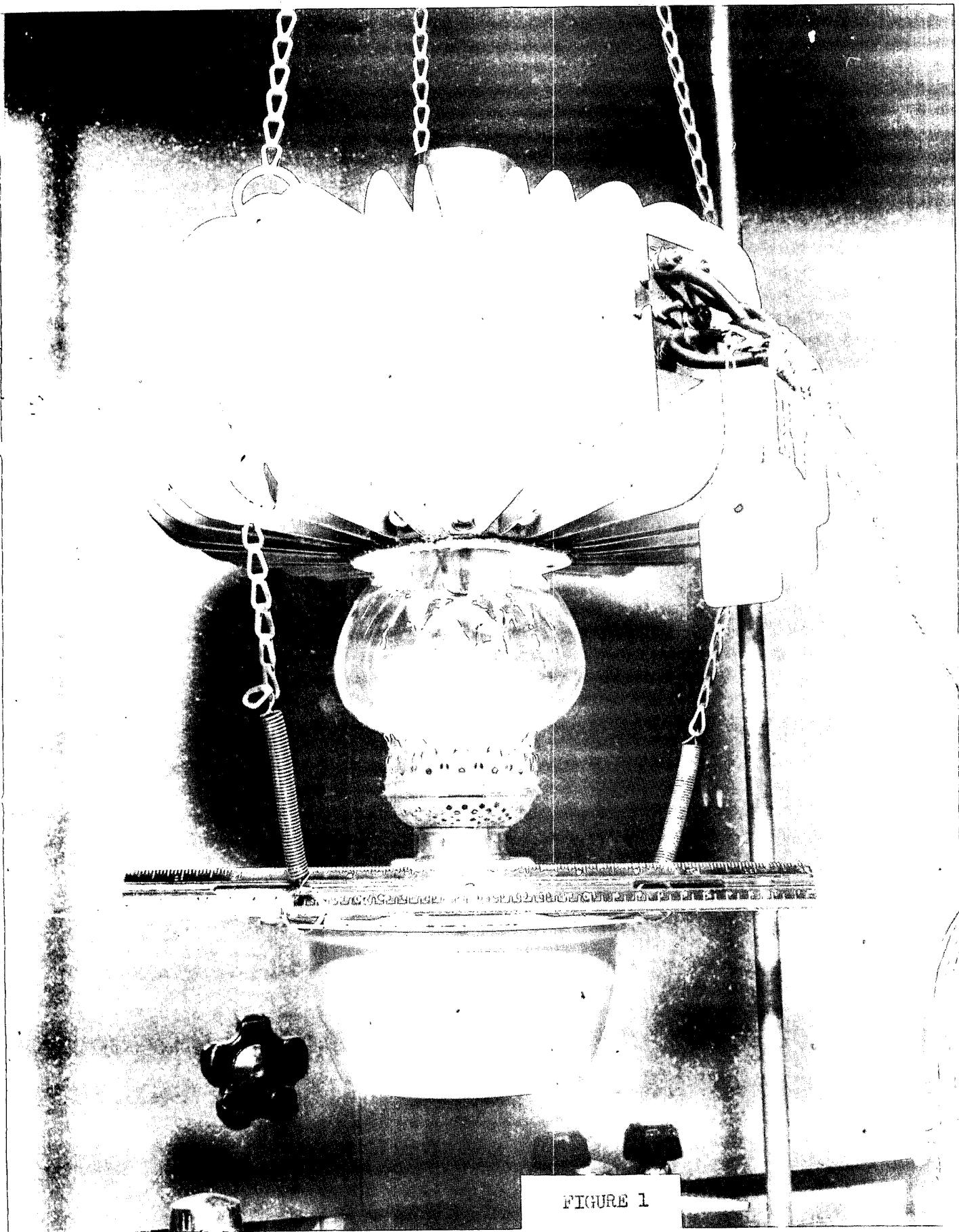
Step 3: Observation of any changes in the properties measured in Step 2 as the generator is operated for protracted periods of time.

Step 4: When no further data on the durability of the device are desired, disassembly of the generator, study of its internal physical arrangement, and analysis of the materials from which it is made.

During this quarter, Steps 1 and 2 have been completed, and Step 3 is in progress.

Figure 1 is a photograph of the kerosene lamp and the thermoelectric generator. The device has been assembled according to instructions, and is shown with the lamp lit. At the upper right of the picture, a terminal block containing five contacts is shown. The contacts are arranged with two horizontal rows of two contacts each, with a single connection at the bottom. The uppermost pair of connections is marked "anode", and the remaining three are numbered 1, 2, and 3. The "anode" circuit is electrically independent of the other three connections, which appear to be taps on a separate generator circuit. The "anode" circuit supplies power for the plate circuit for the radio by means of a vibrator, transformer, and filter network. The appropriate portion of the "1-2-3" circuit powers the filaments. For the particular radio we received, the filament supply is to be connected across contacts 2 and 3.

The radio and the vibrator assembly (with its cover removed) are shown in Figure 2. The vibrator assembly is provided with a small voltmeter to determine the input voltage, and with a switch which can be used to de-energize the vibrator when the thermoelectric generator is operating. Directly behind the vibrator, in the photograph, is an interconnection assembly, providing plug-in



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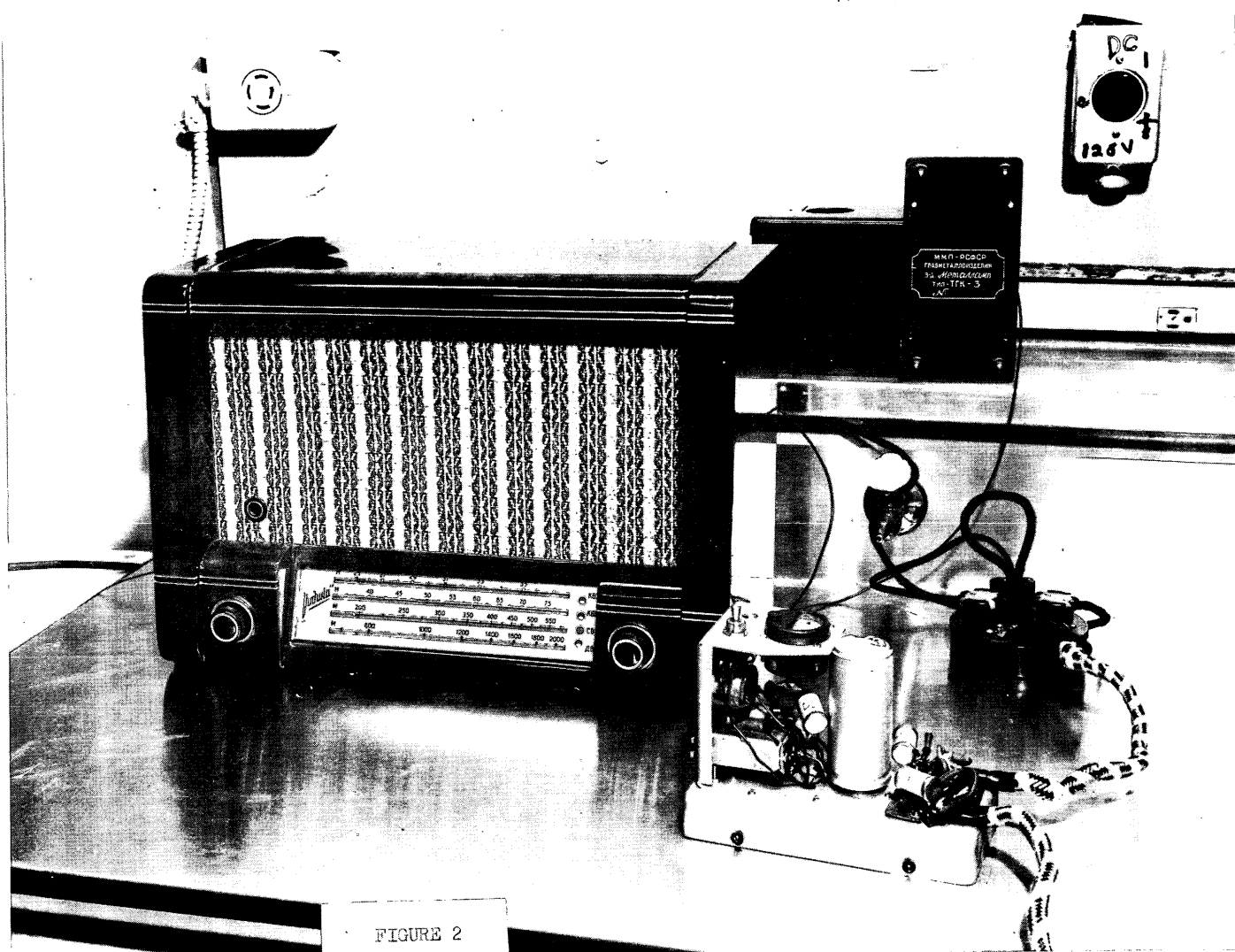


FIGURE 2

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connections among radio, vibrator, and generator. The cover of the vibrator is displayed on the shelf at the back of the laboratory bench. The radio, at the left in the photograph, is a multi-band affair, with provision for long- and short-wave reception, in addition to the standard broadcast band. Not visible on its left side is a switch enabling the user to employ the audio section for phonograph operation, or--a somewhat non-conventional feature--to connect the output from another amplifier directly to the speaker, using none of the electronic portion of the radio. On the lower left of the grille of the radio can be seen the pilot light, which glows faintly when the filaments are heated.

Step 1

With the thermoelectric generator, vibrator, and radio connected according to the instruction manual, the kerosene lantern was lighted, and the time required for the radio to become operative noted. After 2.5 minutes, the output of the generator was sufficient to cause the vibrator to hum. Nine minutes after lighting the lamp, the pilot light on the radio glowed faintly, and the radio began to hum one minute later. The following measurements of the voltage output from the vibrator supply were taken with the plate circuit of the radio disconnected.

TABLE I

EFFECT OF TIME OF OPERATION OF THERMOELECTRIC GENERATOR
ON OPEN-CIRCUIT VOLTAGE OUTPUT FROM VIBRATOR SUPPLY

Time since lighting Generator, <u>minutes</u>	No-load Output from Vibrator Supply, <u>volts</u>
3	50
4	90
10	180
13	210
21	228
40	230

After about ten minutes of operation of the thermoelectric generator, sufficient volume was available from the radio to permit reception of local broadcast stations. Subsequently, some of the more-powerful short-wave stations could be heard, despite the electrostatic shielding afforded by the building in which the experiments were conducted. One might conclude that the entire assembly represents a somewhat complex, but nevertheless quite usable means of providing radio reception in areas lacking other sources of electricity.

Step 2

In order to determine the efficiency of conversion of thermal energy into electrical energy by the thermoelectric generator, as well as the voltage and power outputs as functions of the current drain, the wires shown connected to the generator in Figure 1 were disconnected. In their place, a variable resistor with an ammeter in series were connected across each of the circuits, and provision for simultaneous measurement of voltage also supplied. In addition, measurements of the temperature of the thermoelectric generator at several points were also made by means of thermocouples. The locations of the thermocouples are best described by reference to Figures 3, 4 and 5.

A general view of the top of the generator is shown in Figure 3. The device has been laid on its side and the stack which surmounts the assembly has been removed to provide greater clarity. The photograph shows the cooling fins which are bolted to the exterior of the thermocouple assembly, and the six-membered heat-exchanger inserted in the center of the stack to conduct some of the heat from the waste gases of the kerosene lamp to the hot junctions of the thermocouples. In the background, the instruction manual and the supporting chain can be seen.

A close-up view of the same aspect of the device is portrayed in Figure 4. The method of fastening the cooling fins is evident, and the use of sodium

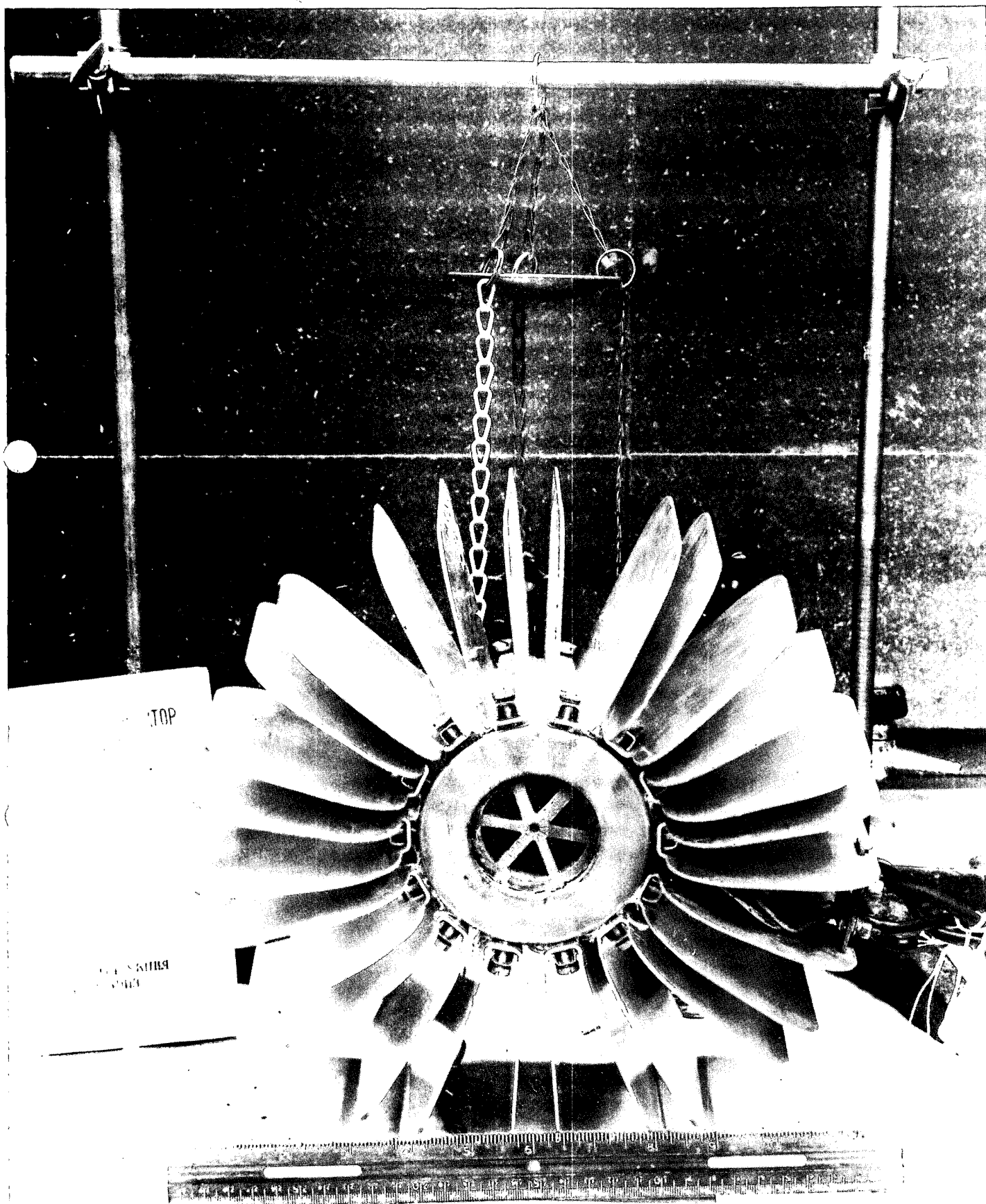


FIGURE 3

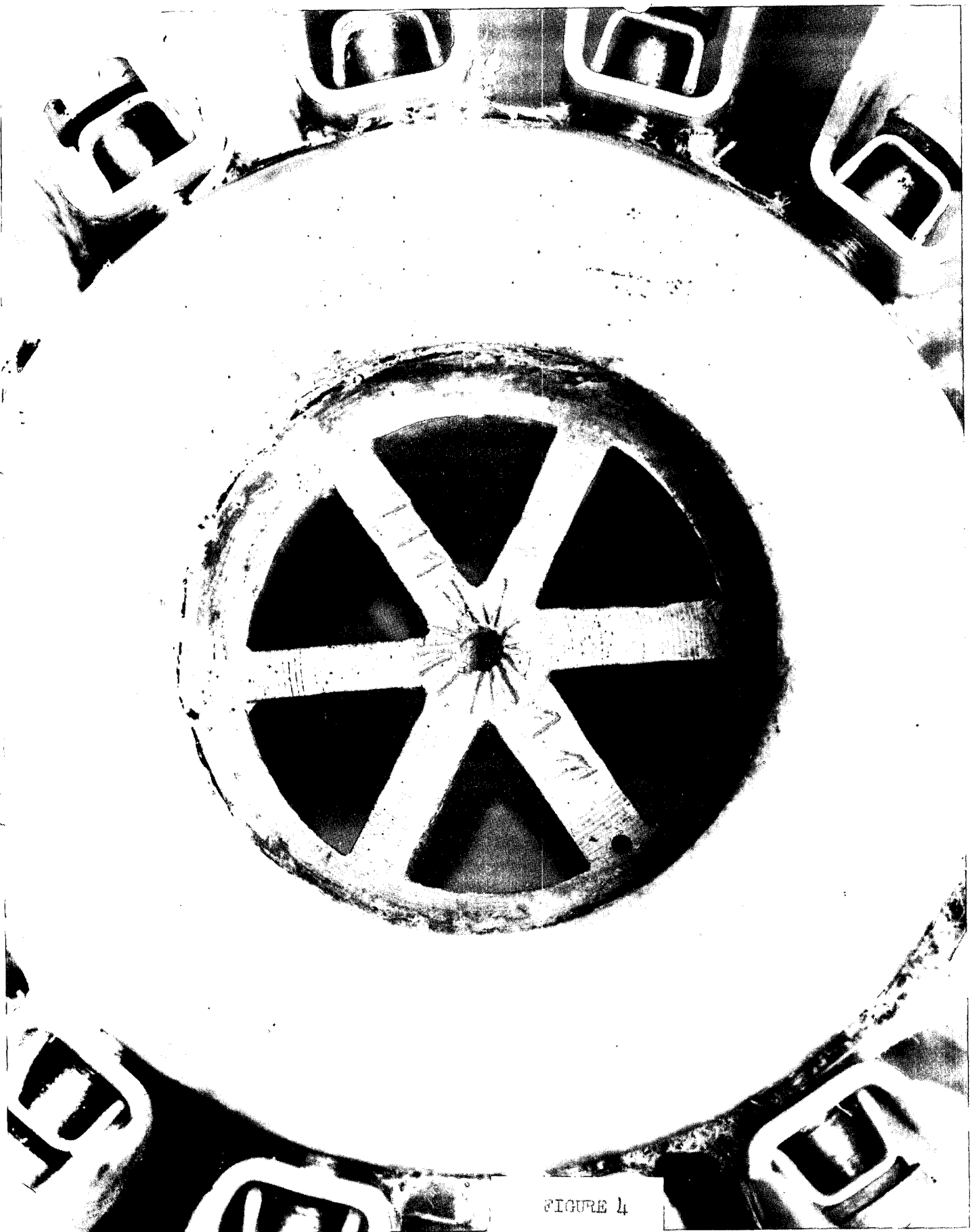


FIGURE 4

silicate to provide a thermal and mechanical bond to the hot junctions is also apparent from the incrustations on the left side of the heat-exchanger. At the lower right portion of the heat-exchanger, a small hole was found. Although its original purpose could not be ascertained, it was used to contain a thermocouple for measurement of the hot-junction temperature at the top of the stack, in the present experiments. Another thermocouple was wedged between the exterior surface of the generator "can" and the cooling fin directly outside the hole in the heat-exchanger. This thermocouple provided measurements of the temperature of the "cold" junctions of the thermoelectric generator.

The location of the thermocouple which was used to measure the hot-junction temperature at the end of the generator nearest the kerosene lamp is shown by the arrow in Figure 5. At the point indicated by the arrow, a small hole was drilled, a thermocouple inserted, and its leads brought up the stack to the outside. This thermocouple does not provide as accurate a measure of the temperature at the hot junctions themselves as does the one at the top of the assembly. The reason for the inaccuracy lies in the location of the hole in the projecting portion of the heat-exchanger. Heat must travel approximately one inch from the thermocouple to the actual hot junction of the generator. At the top of the generator, on the other hand, the spacing between thermocouple and hot junctions is only about one-eighth of an inch.

Figure 5 also shows the asbestos pad against which the lamp chimney is held by three springs, to minimize leakage of the hot gases. Impressions resulting from this contact are clearly visible in the asbestos pad. Some soot can be seen at the center of the heat exchanger. The formation of a soot deposit with the lamp set to produce a maximum amount of hot gas is difficult to prevent, and requires extremely nice adjustment of the lamp wick. With



practice, however, it was found possible to produce a reproducible high temperature (determined by the open-circuit voltage of the generator) without coating the heat-exchanger with the insulating layer of carbon particles.

The results of measurements of voltage and power as functions of current drain, using the kerosene lamp as the source of heat, are displayed graphically in Figures 6 and 7. (Figure 7 is mis-labelled "vibrator circuit", and should be called "filament circuit.") These curves were obtained by lighting the lamp, allowing the open-circuit voltage of the circuit being measured to reach a constant value with the largest flame which would not produce soot, and then measuring voltage and current as the external resistance was reduced. Many of the points have been omitted from the curves, for the sake of clarity, especially since the voltage-current curve was remarkably linear. The power-current curve was obtained from the voltage-current curve, and not by multiplication of the individual observed terminal voltages and currents.

The maximum available power from both circuits is the sum of the two maxima, and is about 2.87 watts. Calculation of the efficiency, with any accuracy, is prohibited by lack of information concerning the rate of heat input to the hot junctions. A rough estimate of the minimum efficiency was obtained, however, by utilizing some of the information given in the instruction manual.

The instruction book accompanying the thermoelectric generator states that kerosene is consumed by the lamp at the rate of 75 grams per hour. With the knowledge that complete combustion of one gram of kerosene results in liberation of 11,006 calories, it is a relatively simple matter to calculate that heat is evolved by the kerosene lamp at a rate of 958 watts. Since it is impossible to ascertain the fraction of this heat which is absorbed by the heat-exchanger, and ultimately by the thermoelectric generator, an assumption must be made. If

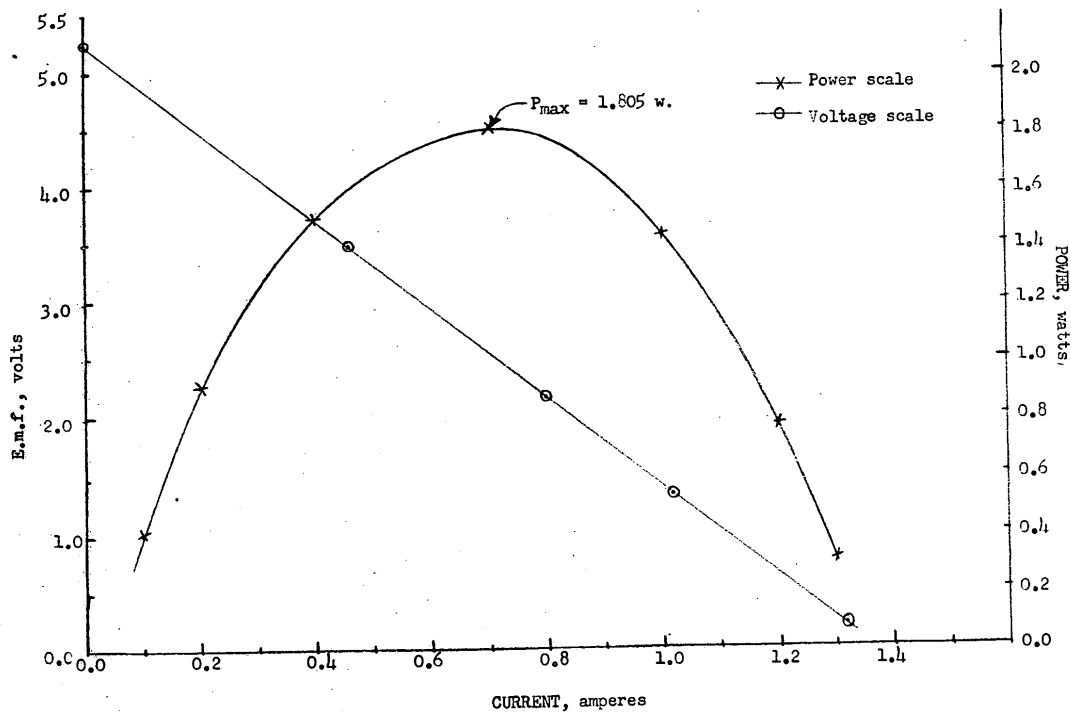


Figure 6: VOLTAGE AND POWER OUTPUT FROM THERMOELECTRIC GENERATOR WITH KEROSENE HEATING
"Anode" circuit

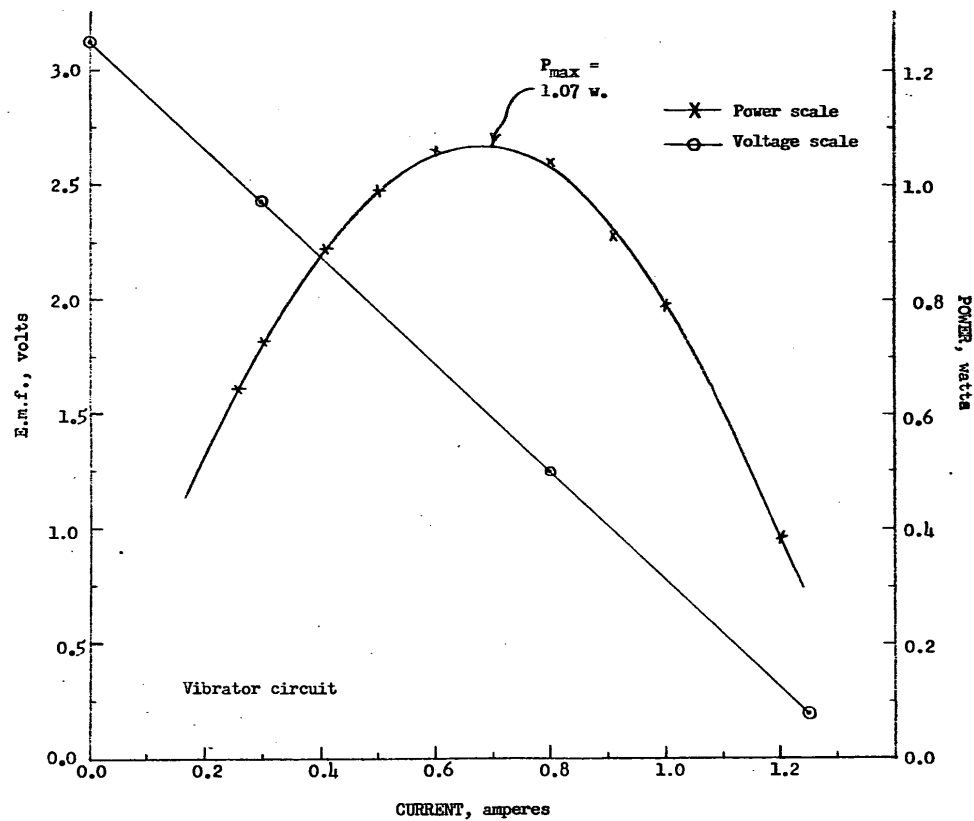


Figure 7: VOLTAGE AND POWER OUTPUT FROM THERMOELECTRIC GENERATOR WITH KEROSENE HEATING

one can assume that fifty per cent of the available heat is actually absorbed, the efficiency is

$$\begin{aligned}\text{Eff.} &= 2.87 \text{ watts output} / 479 \text{ watts input} = 0.0060 \\ &= 0.6\%\end{aligned}$$

The validity of the assumed proportion of the heat absorbed from the stack gases cannot be easily verified. An indication that the heat-exchanger did, in fact, remove a large amount of heat from the stack gases is given by the fact that the temperature at the bottom of the heat-exchanger was 480°C , while that at the top was only 380°C . The "cold" junction was found to maintain a temperature of 80° to 90°C . As mentioned previously, part of the measured difference in temperature between the top and bottom of the heat exchanger may have been due to the location of the thermocouples.

In order to remove any ambiguity from the value of the efficiency, an electric heater was substituted for the kerosene lamp. This consisted of a length of Nichrome wire, wound around the heat-exchanger, but insulated electrically from it. The space inside the heat-exchanger and surrounding its top and bottom was loosely packed with asbestos fibers. In this way, loss of heat from the heating wire by any path save through the thermoelectric generator was reduced to a minimum. The heat input was adjusted so that the open-circuit voltages in the two circuits of the thermoelectric generator were the same as those obtained with the kerosene lamp acting as the source of heat. Three series of measurements were made. In one, voltage and current measurements were made after each change in the external resistance, with no special precaution to assure that thermal equilibrium had been established. In another series, current was allowed to flow for ten minutes after the external resistor had been re-set. In this way, changes in the thermal gradient, due to the Peltier effect,

were allowed to equilibrate with the normal heat-flow. The third series of measurements was made with as brief a period of current drain as could be achieved. The results of these measurements, as well as the results of the measurements made with the kerosene lamp as the heat source are shown in Table II.

TABLE II
EFFECT OF HEAT SOURCE AND METHOD OF MEASUREMENT
ON EFFICIENCY OF THERMOELECTRIC GENERATOR

Property	Heat Source: Kerosene Lamp	Electric Heater		
		No pre- caution in read- ing	Equilib- rium Estab- lished	Instan- taneous Readings
Initial hot-junction temperature, °C	380	376	374	374
Initial cold-junction temperature, °C	80-90	71	75	75
"Anode" circuit E.M.F., volts (I=0)	5.25	5.20	5.20	5.20
Maximum power output, "anode" circuit, watts	1.805	1.77	1.79	1.98
Maximum power output, filament circuit, watts	1.07	0.943	1.01	1.08
Total maximum power output, watts	2.87	2.71	2.80	3.06
Power input to heater, watts	---	298.5	304.5	307.0
Efficiency, per cent	---	0.908	0.918	0.997

It should be noted that there was a delay of five days between taking the first two columns of data with the electric heater. During this time, the thermoelectric generator was maintained at the operating temperature. At the end of the period, it was observed that a larger power input was required to produce the same no-load voltage at the "anode" circuit. This may indicate a change in the properties of the thermocouple materials in the generator as they are heated for extended periods. This will be verified as a part of Step 3.

The effect of the method of measurement of efficiency on the observed values of that property may be seen in the last two columns of Table II. With ten minutes allowed between readings, the efficiency is 0.918%. With no time allowed for the Peltier effect to result in a lower hot-junction temperature, the apparent efficiency is 0.997%. In use, of course, this enhanced efficiency could never be realized, since power is drawn for periods far longer than those used in the measurements.

The low value of observed efficiency resulting when no special precautions were taken during the measurements may be attributed to the sequence of measurement. The open-circuit voltage was determined, followed immediately by the reading of the highest current and smallest voltage. The external resistance was increased step by step, and the correspondingly smaller currents and larger voltages were measured. Since no time was allowed for thermal equilibrium to be reached, the cooling resulting from drawing high currents decreased the temperature difference across the elements of the thermoelectric generator, and a smaller electromotive force than the corresponding equilibrium value was recorded. Evidence for this hypothesis lies in the fact that the open-circuit electromotive force determined immediately after ending a series of measurements was several tenths of a volt less than the value observed at the beginning of the run. After a waiting period of ten minutes, or so, the "before" and "after" values were in good agreement.

A careful measurement of the time required to return to the original open-circuit voltage was made. Both the "anode" and the "filament" circuits were placed in a short-circuit condition for exactly ten minutes. Upon opening the circuits, the open-circuit voltage of the "anode" circuit was measured as a

function of time until the original value (5.20 volts) had been reached. The results are shown in Table III.

TABLE III

TIME REQUIRED FOR ANODE CIRCUIT OPEN-CIRCUIT VOLTAGE TO RESUME
ORIGINAL VALUE AFTER TEN MINUTES SHORT-CIRCUIT OF ENTIRE GENERATOR

Time since Opening Circuit, <u>minutes</u>	"Anode" Open-Circuit, e.m.f., <u>volts</u>
0.0	4.75
0.67	5.00
2.0	5.05
6.0	5.10
12.0	5.15
23.5	5.20 (original value)

Admittedly, the conditions of the experiment whose results are shown in Table III were more severe than would normally exist. Nevertheless, the data show that a maximum of 23.5 minutes would be required for re-establishment of the original temperature gradient.

Step 3

The thermoelectric generator has been allowed to sit at the operating temperature since the completion of the measurements described above. It is planned to wait two weeks, then to measure the efficiency under equilibrium conditions. If any significant change is noted, additional periods of waiting and other measurements are planned. This will extend into the next quarter, and complete results will be reported in the next quarterly report.

2. Study of Russian Periodical Literature

As a portion of the study program, a series of translations from current

Russian periodicals have been purchased and studied. The articles vary from general discussions of the problems of thermoelectricity and Peltier cooling to descriptions of specific devices. Among the latter are Peltier refrigerators, and a dew-point meter using Peltier cooling to produce frost or dew on a mirror, recording the temperature at which the condensation occurs electrically. For the purposes of this program, the most valuable information derived from study of these articles has been the establishment of a means for comparing the effectiveness of thermocouple materials for thermoelectric generators.

According to the Russian articles, a useful "figure of merit" for comparing thermoelements is given by

$$Z = \frac{\alpha^2}{\rho K}$$

where Z is the figure of merit; α is the thermoelectric power, in volts per degree Centigrade; ρ is the resistivity, in ohm-centimeters; and K is the thermal conductivity, in watts per centimeter per degree Centigrade. The units of Z are therefore reciprocal degrees Centigrade.

For comparing completed thermocouples, comprising a positive and a negative thermoelement, the authors suggest

$$Z_{+-} = \frac{(\alpha_+ + \alpha_-)^2}{((\rho_+ K_+)^{1/2} + (\rho_- K_-)^{1/2})^2}$$

in which the plus and minus signs refer to the positive and negative elements of the thermocouple, respectively.

The Russians state, without identifying the material, that they can produce a couple with a value of Z of 2.5×10^{-3} for cooling purposes, and 1.5×10^{-3} for generator applications. This may be compared with a Z of 0.7×10^{-3} for the zinc antimonide-Constantan couple. The highest value of Z for any

material which has been studied and is available in the United States is that of bismuth telluride, use of which is restricted to cooling applications by virtue of its low melting point. The figure of merit for a couple of p-type and n-type bismuth telluride is 1.7×10^{-3} per degree. The figure of merit of Constantan alone is about 0.17×10^{-3} per degree, while zinc antimonide, on the average, has a Z of $1.07 \times 10^{-3} \text{ }^{\circ} \text{C}^{-1}$. One may conclude that Russian investigators have demonstrated that suitable materials exist for doubling the effectiveness of the thermoelectric generator under development in the course of this program, and that a search for materials better than zinc antimonide and Constantan may be warranted.

C. Thermoelectric Generator Development

With the arrival of information concerning preparation and handling of zinc antimonide from our consultant, [] much of the effort in this portion of the program has been devoted to preparation of the material. In addition, equipment for measuring the properties of materials and completed couples has been designed and some has been constructed. The physical dimensions of the individual thermoelements have been chosen, and the performance of the completed generator predicted by calculation from [] data. Despite this heavy activity directed toward production of the device itself, the fire studies described in Quarterly Report No. 1 have been extended to other sources of heat, and the results of these measurements will be reported first.

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1. Fire Studies

Using the copper-block calorimeters described in Quarterly Report No. 1, measurements of the thermal power available to them at 350°C from several additional heat sources were made. For the sake of completeness, the new results are combined with those previously reported, in Table IV. In one or two

cases, the rate of heat absorption by the calorimeter was measured at other temperatures than 350° , hence the temperature of measurement is recorded in every instance.

TABLE IV

THERMAL POWER RECEIVED BY COPPER CALORIMETER FROM VARIOUS SOURCES

Heat Source	Power Absorbed, watts	Temperature $^{\circ}\text{C}.$
Laboratory gas burner (Fisher type)	1163	350
Electric hot-plate, 2000-watt input	988	350
Wood fire	656	350
Wood fire with paper added	926	460^1
Stove-type gas burner, using natural gas	757	350
Charcoal fire	931	200
	700	280
	550	347^2
Large gasoline camp stove (Coleman)	562	350
Small gasoline camp stove (J. C. Higgins)	418	350

¹Paper was added to the dying wood fire when the calorimeter was at a temperature of $400^{\circ}\text{C}.$

²The measurement was discontinued at this temperature because the fire was dying when the calorimeter had reached a temperature of $332^{\circ}\text{C}.$

It is evident from Table IV that most of the sources of heat which will supply 1000 watts to the bottom of the thermoelectric generator when its temperature is 350°C would not be available under conditions requiring its use. On the other hand, wood fires, paper fires, gas stoves, and large gasoline burners all will supply about 600 watts, or more, at this temperature. Even the charcoal fire would supply more than 90% of this heat flow. Because of

this information, it was requested of the representatives of the Customer, on October 25, 1956, that the design of the thermoelectric generator be based on a heat flow of 600 watts, rather than 1000 watts, as originally proposed. The permission was granted.

Although the heat sources listed in Table IV are fairly representative of those frequently available in this part of the country, the list is incomplete. It has been planned to measure the thermal power available from a coal-burning kitchen stove, and, possibly, a kerosene-burning kitchen stove. In addition, fires of peat, lignite, and cow-dung are to be investigated, rounding out the projected list. The fire studies have been temporarily discontinued, however, in order to devote more time to other aspects of thermoelectric generator production.

2. Zinc Antimonide Production

Almost immediately upon the arrival of the written information concerning preparation of zinc antimonide, the positive element in the thermocouples to be used for the thermoelectric generator, materials were ordered, and construction of equipment begun. As suggested by [] "Lone Star" brand antimony was STAT ordered from the Texas Mining and Smelting Co., of Laredo, Texas. This material is guaranteed to contain no less than 99.8% antimony, and has been found by

[] typically to contain the following impurities:

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Iron:	0.025%
Sulfur:	0.023%
Arsenic:	0.040%
Copper:	0.010%

The material was ordered re-cast from 224-pound ingots into ten-inch pieces, three-eighths of an inch in diameter. Since sulfur is used as a flux to prevent oxidation during the re-casting operation, it is likely that the sulfur content of the material received was higher than stated above.

The Belmont Smelting and Refining Works, of Brooklyn, New York, was the source of zinc, as well as of tin to be used in "doping" the zinc antimonide. Before being re-cast into half-inch bars, ten inches long, the zinc was 99.99+% pure. Major impurities are lead and cadmium (0.001% each), with a trace of iron. Formation of a "skin" of zinc oxide on the surface of the bars is unavoidable if they are allowed to remain in the air for protracted periods.

Since the "doping" compound, added to the zinc antimonide to decrease its electrical resistivity and to improve its mechanical integrity, forms less than two per cent of the finished thermoelement material, extreme purity is not absolutely essential in its ingredients. These, in addition to the tin mentioned above, are bismuth and silver. The purity of the tin was 99.98%. Cerro de Pasco Company of New York City, which supplied the bismuth, certified its purity at 99.999%. Sheet silver of high quality was available from supplies in the laboratory. Supplied as "fine silver", it is known to be 99.9+% pure.

The doping compound was made by melting together one part of silver and two parts each of bismuth and tin. After thorough mixing at a temperature between 400° and 500°C, the alloy was run into a heated Pyrex tube with an internal diameter of about 2 millimeters. The resulting long, slender bar may easily be cut to provide the small amounts of doping compound needed for preparation of doped zinc antimonide. Two parts by weight of doping compound is added to each hundred parts of stoichiometric zinc antimonide. A typical small batch would be made up in the following proportions, with the precision of weighing held to a ten-milligram tolerance for the major constituents and a one-milligram tolerance for the doping compound:

Zinc:	65.38 g
Antimony:	121.76 g
Doping compound:	3.743 g

Melting of the entire mixture takes place at 610°C in an evacuated Pyrex tube which is placed in an electrically-heated furnace. The furnace is so constructed that it can be placed in a horizontal or a vertical position, or rocked, periodically, to facilitate mixing of the ingredients. The mixture is maintained at 610° for about one hour, to assure complete homogeneity, and then the furnace is placed in a vertical position. At this juncture, the electrical input to the furnace is adjusted to provide a temperature of 480°C , and this temperature is maintained within five degrees for a period of at least 24 hours. The purpose of holding the solid zinc antimonide (melting point: about 565°C) at 480° for this length of time is to provide annealing of its crystals. At best, the material is quite brittle. Annealing tends to reduce this undesirable property to a minimum.

In order to test the operation of the furnace, its associated electrical equipment, the technique of sealing the materials in the evacuated Pyrex tube, and the usefulness of the fixture designed to hold the tube during the melting and annealing processes, a "dry run" was made, using only zinc and antimony as the charged materials. Several defects in the operation of the equipment were noted, and steps to correct them have been taken. Most serious of these was the softening of the Pyrex tube under the influence of the vacuum and the high temperature. It collapsed, making removal from the furnace difficult and yielding a distorted casting of ZnSb . It has been decided that use of Vycor (96% silica) tubing for future work is essential, since its 1500-degree softening point is well above the range of temperatures to be encountered in this work.

The most serious difficulty encountered in the dry run was, unfortunately, not one of technique or equipment. It was observed that a large amount of black dross appeared on the surface of the ingot of zinc antimonide. In addition,

despite the annealing, the material was severely cracked throughout, with foreign material lining the cracks. It was obvious that the impurity could not be held in place and mechanical integrity restored by addition of two per cent of doping compound. Consequently, it was decided to assure utmost purity of the starting materials before melting.

The technique chosen was zone-melting, or zone-refining, because of the ready availability of the apparatus for the process in the laboratory. The method consists of placing a bar of the material to be purified in a boat which rests in a quartz tube. Water-cooled coils of tubing, connected to an induction heater, and spaced about four inches apart, surround the quartz tube. The input to the coils is adjusted so that the material to be purified is molten in the portions surrounded by coils, and solid in the spaces between them. The coils are moved slowly along the axis of the tube, and the molten zones move with them. The driving mechanism is so constructed that the coils return nearly instantaneously to their original positions after traversing a distance equal to the space between them. In this manner, the effect of continuously moving molten zones through the material is produced. Many of the impurities remain in the molten phase as the process continues. After several passes of the molten zone through the material, they are concentrated at one end of the bar, leaving material of high purity at the opposite end. This process has been used to refine semiconductor materials to an impurity level of less than one part in a billion.

Since the purity of the antimony, as supplied, was one-tenth that of the zinc, it was selected as the first material to be purified. It was found that large crystals of antimony result from holding it molten at red heat for three to four hours, while in a stream of gas consisting of 90% argon and 10% hydrogen,

then allowing solid zones to form and be traversed by molten zones for four or five hours at the rate of eight inches per hour. The gas is allowed to flow at all times, to prevent oxidation. An additional function of the gas stream appears to be to reduce antimony sulfide to elemental sulfur or to hydrogen sulfide, and to remove it in either form. The zone-refining method has produced hemicylindrical bars of shiny, silvery antimony, about five inches long and half an inch wide, and consisting of three or four crystals for their entire length. Since ease of crystal growth is a rough measure of purity, and since the material, as received, contained no crystals larger than one by five millimeters, the purity of the material may be taken to be at least an order of magnitude higher than before processing. Removal of copper, though not contributing to the mechanical stability of zinc antimonide, may improve the electrical properties, especially the thermoelectric power.

Zone-refining of zinc was not found to be accomplished with as great ease as was the case with antimony. Although some increase in crystal size was observed, it was not sufficient to warrant the effort. In addition, by re-casting the zinc just prior to its use, it is felt that the formation of zinc oxide can be nearly eliminated. It is this impurity in the zinc which is most objectionable. In the case of the antimony, sulfur, copper, and arsenic are all undesirable, and all should be capable of removal by zone-refining.

As the quarter drew to a close, the supply of purified materials was nearly adequate to permit preparation of several batches of doped zinc antimonide. Vycor tubing for enclosing the ingot was on hand. It is expected that the next quarter will see preparation of sound ingots of material suitable to serve as the positive elements of thermocouples for use in the thermoelectric generator.

3. Design of Thermoelements

Along with information concerning preparation of thermoelements,

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consultation report described in detail methods for designing completed thermocouples with the optimum dimensions. Her method uses a "form factor", the purpose of which is to achieve a balance among the thermal and electrical conductivities of the positive and negative thermoelements. To illustrate the use of the form factor, the calculations leading to the design of the thermocouples are shown in some detail below.

In order to ascertain the physical proportions of the elements of the individual thermocouples, suggests the following method of selection of their optimum dimensions: STAT

$$FF = \frac{(S/L)_+}{(S/L)_-} = \frac{(K_- \rho_+)^{1/2}}{(K_+ \rho_-)^{1/2}}$$

in which the symbols have the following significance:

FF is the "form factor";
S is the cross-sectional area of an element in square centimeters;
L is the length of the element in centimeters;
K is the specific heat conductivity in watts/centimeter-°C;
 ρ is the resistivity in ohm-centimeters;
and the subscripts, + and - refer to the sign of the thermoelectric power of the element under consideration.

The data used below represent average values for over 200 samples of zinc antimonide, and the published values of the Driver-Harris Corporation for their "Advance" brand of Constantan. Substituting these data into the form-factor equation above, one obtains STAT

$$FF = \frac{(0.218 \times 0.0025)^{1/2}}{(0.015 \times 49 \times 10^{-6})^{1/2}} = 27.25$$

The ratio of area to length of the zinc antimonide must therefore be 27.25 times that of the Advance (or Constantan).

For ease of preparation, it has been decided to cast the zinc antimonide in Vycor tubes, using a vacuum-casting technique. A convenient and available size of Vycor tubing has an internal diameter of 5 millimeters. The length of the couples (both elements) has been selected as 5 millimeters. The length is a compromise between the desire to construct a thermoelectric generator in as compact form as is possible and the necessity for handling the individual elements with ease. With these dimensions, the area/length ratio for the positive thermoelement becomes

$$(S/L)_+ = (3.14 \times (0.5)^2) / (4 \times 0.5) = 0.393 \text{ cm.}$$

Therefore, for the Advance, the ratio is

$$(S/L)_- = (S/L)_+ / FF = 0.393 / 27.25 = 0.0144 \text{ cm.}$$

Since both elements are to be the same length, 0.5 cm,

$$S_- = L(0.0144 \text{ cm}) = 0.5 \times 0.0144 \text{ cm}^2 = 0.00720 \text{ cm}^2$$

or
$$S_- = 0.00112 \text{ in}^2$$

This corresponds closely to the cross-sectional area of Advance ribbon, nominally 0.125 inch wide and 0.010 inch thick.

With the dimensions of the individual elements specified, it remains to determine their expected performance. The resistance of the Advance element is 0.00323 ohms, and that of the zinc antimonide element is 0.00636 ohms, giving a total resistance of 0.00959 ohms per couple.

Under conditions of no electrical load, the electromotive force developed by a thermocouple is given by the product of the thermoelectric power and the temperature difference between the hot and cold junctions. The approximate thermoelectric power of the zinc antimonide-Advance couple is 250 microvolts per degree Centigrade. The temperature difference between the hot and cold junctions has been estimated to be 230°C, with allowances being made for thermal

impedances of the electrical insulation and other portions of the assembled generator. (The un-corrected temperature difference would be $350^{\circ} - 100^{\circ} = 250^{\circ}$.) The open-circuit voltage is therefore

$$\text{O.C.V.} = 250 \times 10^{-6} \times 230 = 57.5 \text{ millivolts.}$$

For practical purposes, conditions of maximum power transfer to a load exist when the internal and external resistances are equal, when the output voltage is half that under open-circuit conditions, or 28.75 millivolts.

The current drawn under conditions of maximum power transfer is given by Ohm's Law:

$$I = E/R = 0.02875 \text{ v} / 0.00959 \text{ ohms} = 3.00 \text{ amp.}$$

This current is independent of the number of couples in the completed thermoelectric generator, provided the conditions for maximum power-transfer are met. Knowing the current under these conditions, it becomes possible to calculate the number of couples required to utilize all the electrical energy which can be converted from 600 thermal watts.

The useful power obtainable by use of zinc antimonide-Advance thermocouples across which a 230-degree thermal gradient exists is 3.4% of the thermal power flowing into the thermocouples, according to report. From a flow of 600 watts, 20.4 watts can therefore be converted to useful electrical energy. Having ascertained that the current flowing will be 3.00 amperes, it is easily seen that the voltage required is

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$$E = P/I = 20.4 \text{ w} / 3.00 \text{ amp} = 6.80 \text{ volts.}$$

This can be obtained, under conditions of maximum power transfer, using 237 thermocouples in series, each with an output of 28.75 millivolts. With no current drawn, the electromotive force of the generator would be twice that above, or 13.60 volts.

It should be pointed out that the calculation of the number of thermocouples shown above did not take into account the detailed heat balances required by rigorous thermodynamics. Suffice it to say that the exact calculation, while far more tedious, yields a number of thermocouples which differs by only about five per cent from the result above.

The 237 thermocouples could easily be fit into an assembly such as that depicted in the previous Quarterly Report. Allowing one square centimeter per couple, there would still be sufficient room between the two "pans" for a thermally-operated switch, even if the diameter of the pans were only eight inches. A thermally-operated switch would serve the purpose of not closing the external circuit unless the temperature difference were sufficient to provide the minimum desired output voltage.

4. Testing Equipment

It is essential that the quality of the zinc antimonide and of the assembled thermocouples be maintained at the highest possible level. In order to accomplish this, data concerning resistivity, thermal conductivity, thermoelectric power, and efficiency of conversion of thermal into electrical energy are required. consulting report contains sketches and photographs STAT of the equipment she employed for the purpose. Modifications have been made in her designs to suit the dimensions of the devices and materials with which this study is concerned.

Several of the sketches of the modified equipments have been completed, and the resistivity meter for use at room temperature has been completed. It is shown being tested in Figure 8, in the center of the photograph, on the table. The specimen whose electrical resistivity is to be determined is clamped in the vise, between jaws covered with copper gauze, to assure good electrical

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FIGURE 8

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contact. A measured current is passed through the length of the specimen, and the voltage drop between two movable needle probes measured with a potentiometer. The spacing between the probes, as well as their position along the specimen, may be changed at will.

If the current and voltage drop across a given length are known, application of Ohm's Law leads to the resistance along that length. Assuming that the specimen has a known, uniform cross-sectional area, the resistivity is calculated by application of the formula

$$\rho = \frac{R A}{L}$$

where ρ is the resistivity, in ohm-cm;
 R is the measured resistance, in ohms;
 A is the cross-sectional area, in square centimeters;
 and L is the distance between the probes, in centimeters.

Measurement of the resistivity at several places along a given specimen gives a good indication of its homogeneity.

During the next quarter, the other pieces of testing equipment will be completed and described in the report covering that period.

D. Development of Gas Activated Battery

1. Introduction

This report describes initial progress in a program for the design of a gas activated solid electrolyte battery system. This program was suspended before the end of the quarter because of the necessity for taking up other work.

The characteristics of the proposed battery are described in a proposal for [REDACTED]

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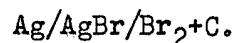
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[REDACTED] and are reviewed briefly here. A solid electrolyte system comprised of eleven

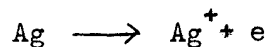
large area ($\sim 70 \text{ cm}^2$) Ag/AgBr/Br₂+C cells in series, with the bromine pressure at about one-third of an atmosphere, is expected to yield a 10 volt battery capable of delivering about 7 milliamperes at room temperature and having a theoretical capacity of 1 ampere-hour. It was proposed that this battery and its accompanying liquid bromine reservoir could be made to fit into a cylinder one inch in diameter and one inch high.

2. Design Considerations

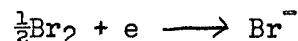
The first requirement of the proposed battery to be investigated was its current capacity. This can best be discussed by referring to Figure 9 where a schematic arrangement of cells to form a battery is shown. (It is pointed out that the geometrical arrangement shown here is not the one contemplated for use in making the battery of the proposed volume but is used for purposes of illustration and also to investigate some basic properties for application to the final design.) It is seen that the cells making up the battery are of the system



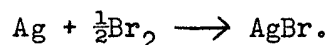
The carbon powder has the functions of making electrical contact between cells and of providing a porous medium for the diffusion of bromine gas to the AgBr/C+Br₂ interface. The bromine resistant, electrically conducting layer prevents the bromine gas from tarnishing the underlying silver and thus produce two cells opposing one another. The anode reaction

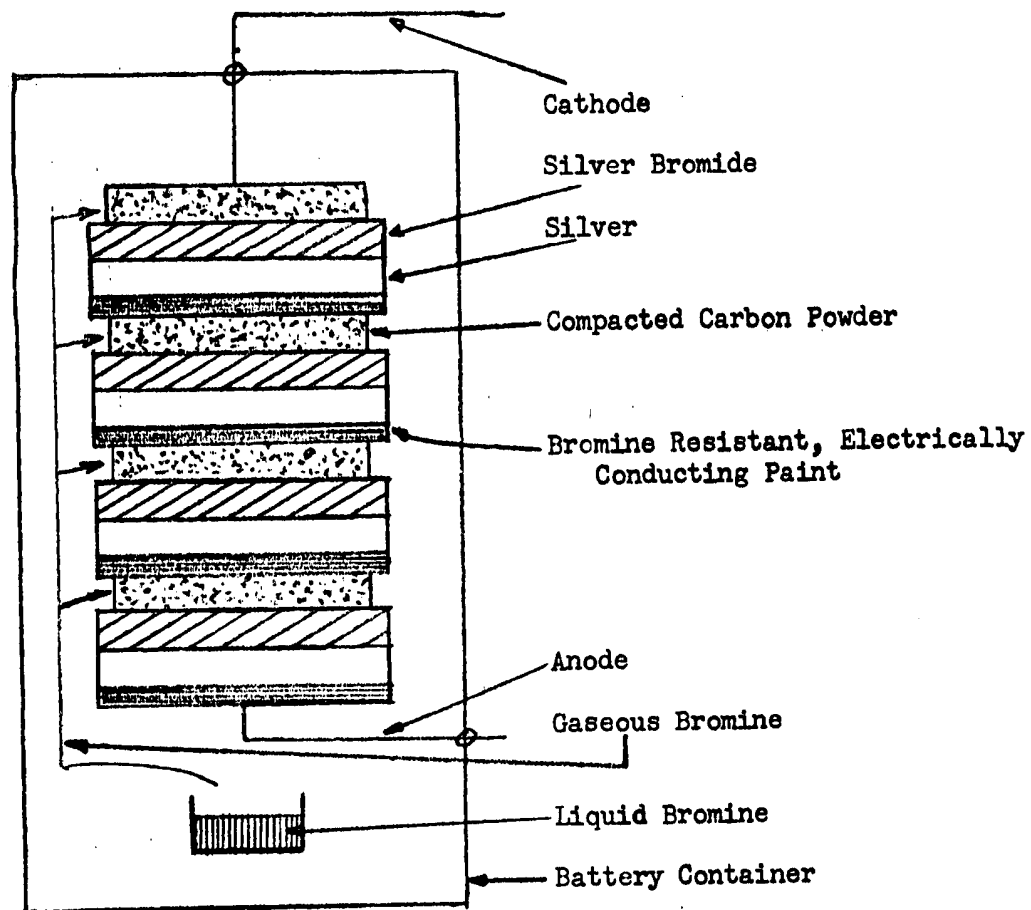


takes place at the Ag/AgBr interface and the cathode reaction



takes place at the AgBr/C + Br₂ interface and together make up the net cell reaction





SCHEMATIC ILLUSTRATION OF BROMINE GAS-ACTIVATED BATTERY

FIGURE 9

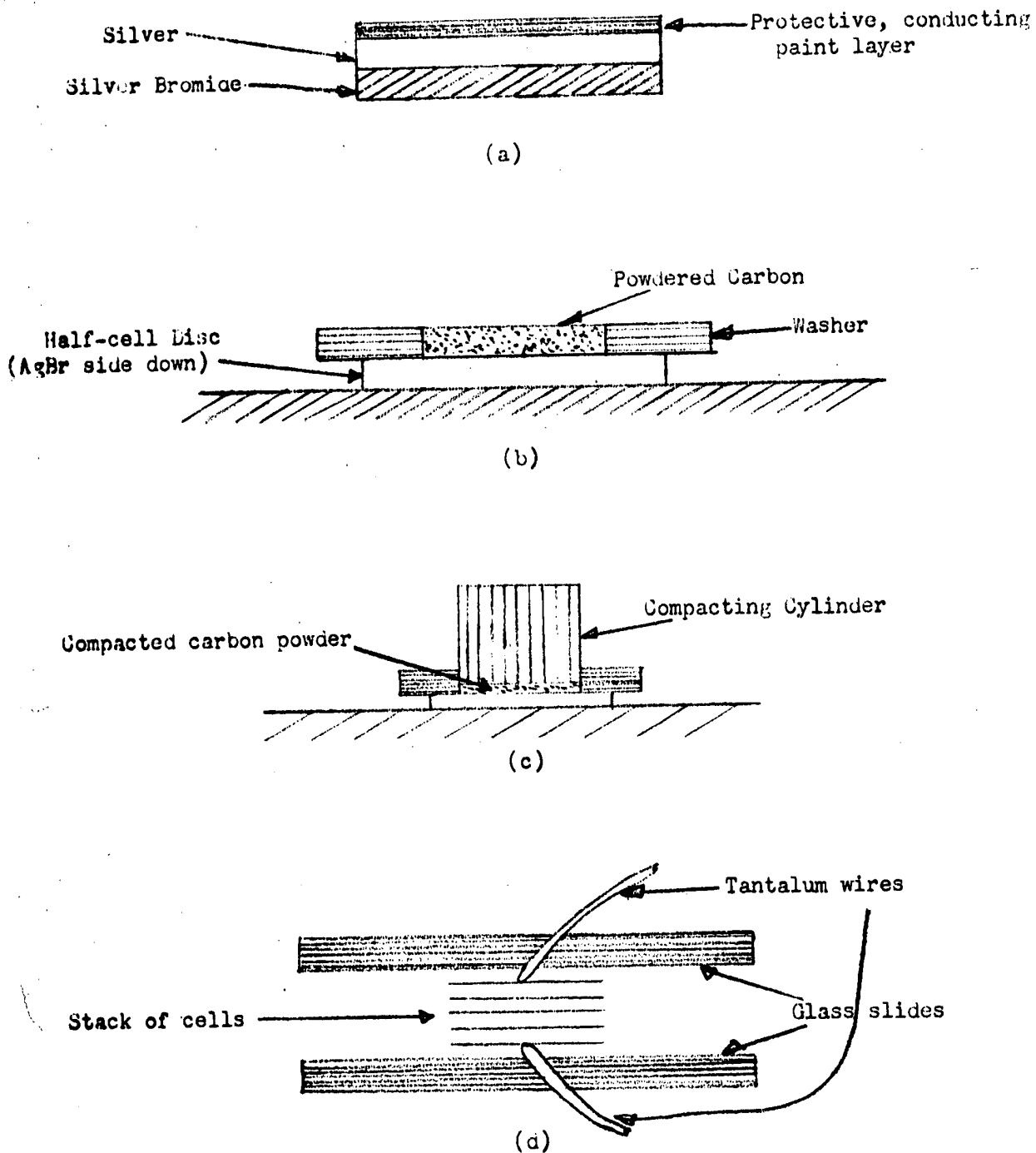
By considering the equation for the cathode reaction it is clear that a sufficient amount of bromine gas per unit time must reach the $\text{AgBr/C} + \text{Br}_2$ interface to maintain a given rate of discharge in the cell. To gain an estimate of the necessary dimensions of the carbon powder layer to enable the desired rate of bromine transport through it to take place, several experimental batteries of from three to five cells were constructed.

Two other factors are known to affect the current capacity of the cells by means of their influence on the internal resistance. These factors are the conductivity of the silver bromide electrolyte layer and the contact resistance between the carbon powder and the silver bromide layer. Although these two factors are being temporarily disregarded, further measurements will have to be made on batteries in which variations have been made in compacting pressure on the carbon, and thickness of the silver bromide electrolyte layer, in order to determine to what extent they affect the internal resistance of the batteries.

3. Experimental Procedures

In Figure 10 are illustrated the steps taken in making up the cells and assembling them in batteries. This was done with relatively crude equipment while waiting for more precise fixtures to be made. The "half-cell" material shown in Figure 10 a) was made up by punching $3/4$ " diameter discs from a brominated silver sheet. This sheet was originally 0.001" thick and was brominated until about 0.0005" of the silver was converted to silver bromide. The silver side of this sheet was covered with a bromine resistant, electrically conducting paint. STAT

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Figure 10 b) illustrates the initial step in making up a cell. The $3/4$ " diameter "half-cell" disc was placed on a clean surface with the silver bromide side down. A brass washer ($9/16$ " i.d.,



SCHEMATIC ILLUSTRATION OF STEPS IN ASSEMBLING A BATTERY

Figure 10

1/16" thick) was placed on top of the disc and held in place with a clamp. The exposed area of the disc within the washer was covered with a very light coat of the protective paint and while this paint was still wet it was dusted with Shawinigan carbon. The washer was then filled to its top with additional carbon over the dusted-on layer. This is the point in the procedure shown in Figure 10 b). The carbon powder was then pressed down with a rod fitting snugly inside the washer. The resultant compacted layer was about 0.010" to 0.020" thick. This step is shown in Figure 10 c). The individual cells so formed were assembled into a battery as shown in Figure 10 d). In this illustration three cells are held between two microscope slides with a conventional hose clamp. Tantalum wires wrapped around the microscope slides and pressed against the compacted carbon discs to provide the anode and cathode leads.

Batteries made in this fashion were placed in 8 oz. jars together with some liquid bromine. The jars were sealed at the top with flat glass plates and Kel-F No. 90 Fluorocarbon stopcock grease.

These batteries were run under short circuit conditions to get some idea of their current capacities. Periodically the open circuit voltage was measured with a vacuum tube voltmeter. After about five hours of this treatment the batteries failed as might be expected under the short circuit conditions. (It was anticipated that further tests under load would be made on batteries assembled with the more precise fixtures to be made.)

Some very qualitative idea of the internal resistances of these batteries may be made by considering the maximum voltages and currents delivered during their lifetime. As examples a three cell and a five cell battery may be considered. For the three cell battery the values were 2.83 V and 5.4×10^{-4} amp. Let R_B be the internal resistance of this battery. Thus

$$R_B = \frac{83}{5.4 \times 10^{-4}} = 0.53 \times 10^4 = 5300 \Omega$$

The internal resistance R_c of each cell is

$$R_c = \frac{5300}{3} = 1767 \Omega$$

The area of each cell is 1.6 cm^2 . Normalizing to a 1 cm^2 area the internal resistance R'_c is

$$R'_c = (1.6) (1767) \approx 2800 \Omega$$

Similar calculations on the five cell battery whose maximum values were 4.49 V and $6.6 \times 10^{-4} \text{ amp.}$ give the following results:

$$R_B = 6800 \Omega ; R_c = 1360 \Omega ; R'_c \approx 2200 \Omega$$

These values may be compared with those for the proposed battery of eleven cells each of 70 cm^2 area delivering $7 \times 10^{-3} \text{ amp.}$ at 10 volts. The internal resistance of this battery was assumed to be about 140Ω . Following the above calculations the following results are obtained:

$$R_B = 140 \Omega ; R_c = 12.7 \Omega ; R'_c = 890 \Omega$$

Of course the R'_c values are the ones to be used as a basis for comparison. It is seen that these values of the internal resistance are much greater for the experimental cells than for the proposed cell. When it is taken into consideration that the carbon layers in the experimental cells are $0.010'' - 0.020''$ thick as compared with a thickness of $0.002''$ in the proposed cell it is clear that it is necessary to investigate also the effect on internal resistance of the additional factors described previously, namely, resistance of the silver bromide electrolyte layer and contact resistance between the carbon layer and the silver bromide layer. The thickness of the silver bromide layer can be decreased and the compacting pressure on the carbon layer can be increased as steps in decreasing the internal resistance caused by these two factors. Of course compacting the carbon more densely will decrease the permeability of this layer to the bromine, but the relative importance of these factors will have to be determined by experiment.

V. CONCLUSIONS

A. The foreign thermoelectric generator being studied in this laboratory operates with little difficulty, using the kerosene lamp intended as its heat source. Its measured efficiency was between 0.91 and 0.92 per cent. There is the possibility, which is being investigated, that this value may change upon prolonged heating of the thermoelements. X

B. From study of the Russian periodical literature, and from discussion with those who have attended their oral presentations, it is inferred that the Russians possess a large amount of theoretical and practical knowledge in the field of thermoelectric power generation and Peltier cooling. Their "figure of merit" for comparison of the performance of thermoelements and thermocouples has been quite useful in our own studies. In addition, they appear to have materials for conversion of thermal into electrical power almost twice as effective as those being studied in this country. X

C. Transfer of 1000 watts from heat sources available in the field to a copper calorimeter is extremely difficult in the temperature range near 350°C. Transfer of 600 watts from these sources, under the same conditions, is feasible, and has led to modification of the design of the thermoelectric generator being developed as part of this work. A generator using 237 thermocouples of zinc antimonide and Advance should absorb heat from these sources at the 600-watt rate, yielding a maximum output of 20.4 watts. At maximum power output, the thermoelectric generator is predicted to yield 3.00 amperes at 6.80 volts. ✓
The open-circuit electromotive force is 13.60 volts.

D. Purity in excess of 99.8 per cent is required of zinc and antimony, if they are to be used for production of zinc antimonide of good mechanical integrity. Zone-refining results in at least a ten-fold improvement in the ✓

purity of the antimony, but has little obvious effect upon the zinc. The quality of these substances, as well as of the tin, bismuth, and silver additives is now at a sufficiently-high level to permit preparation of mechanically-sound zinc antimonide.

E. Construction of a fixture for measurement of the resistivity of zinc antimonide has been completed. Design of equipment for measurement of specific heat conductivity and thermoelectric power of thermoelements, and efficiency of completed thermocouples is nearly complete. ✓

F. Several bromine gas activated batteries of preliminary experimental design (of from 3 to 5 cells) made up of the $\text{Ag}/\text{AgBr}/\text{Br}_2 + \text{C}$ system were subjected to short circuit current capacity measurements. The internal resistance of the cells in these batteries, normalized to 1 cm^2 in area, was about 2500Ω as compared with 9100Ω for the proposed battery. Due to the press of other tasks, the work was discontinued at this point. Although the above results are encouraging, measurements should be made on more precisely assembled batteries whose geometry, dimensions and conditions of assembly, such as humidity, are better controlled. ✓

VI. PLANS FOR NEXT QUARTER

It is doubtful that time will permit expansion of the study phase of the program to a great extent, during the next quarter. The study of the properties of the foreign thermoelectric generator after prolonged heating will be continued. When these measurements are completed, the device will be disassembled, and its parts subjected to chemical and spectroscopic analysis. Upon completion of the entire investigation, a separate report, covering the thermoelectric generator, will be issued. The remainder of the effort devoted to the study program will be channelled in the direction of continuing the study of the literature.

The vast majority of the work of the next quarter will be directed toward production and testing of thermocouples. This will include laboratory preparation of zinc antimonide and development of means for casting it to the desired shape for use as thermoelements. Construction of testing equipment will be completed. If time permits, several techniques for assembly of thermocouples will be investigated. A non-electrical model of the thermoelectric generator will be constructed, having identical thermal properties to the generator itself. It is hoped that experiments performed with this model will yield information useful for improving the design of the thermoelectric generator.

Since the services of the members of the staff who worked on the gas-activated-battery portion of the program during this quarter will no longer be available, it is not likely that progress in this area will be great.

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